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*P.A. Glaude, H.J. Curran, W.J. Pitz, C.K. Westbrook*

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# Kinetic Study of the Combustion of Phosphorus Containing Species

P.A. Glaude, H.J. Curran, W.J. Pitz and C.K. Westbrook  
Lawrence Livermore National Laboratory, Livermore, CA 94551

## Abstract

The combustion of organophosphorus compounds is of great interest for the incineration of chemical warfare agent and their use in flame inhibition as halon replacement. The thermochemical data of these species and the reactions involved at high temperature are not well known, despite some recent experimental studies. With BAC-MP4 *ab initio* estimations as a basis and semi-empirical estimations for many new compounds, the thermochemistry of organophosphorus compounds is studied. New group additivity values are proposed for enthalpies of formation at 298K, entropies and heat capacities of species involving pentavalent phosphorus bonded to carbon, hydrogen, oxygen, fluorine, nitrogen and sulfur atoms.

The kinetic of unimolecular elimination is investigated by modeling pyrolysis experiments of DEMP, TEP and DIMP. A new combustion mechanism is described and applied to the modeling of DMMP reaction in a  $H_2/O_2$  flame.

## Introduction

New needs have appeared for in recent years in the knowledge of thermochemistry and reactions of organophosphorus compounds. A first interest is related to the elimination of chemicals such as pesticides or obsolete chemical warfare agents for which incineration is currently used. Another interest is that phosphorus containing species may have high efficiencies as inhibitors in combustion. Already used as fire-retardant in some polymers, they could be of interest in the replacement of halons [1-3]. This capacity to catalyze radicals recombination could be used also to improve the efficiency of aircraft nozzles by allowing increased heat release into the nozzle and minimizing the energy loss in the exhaust gas [4-5].

Detailed chemical mechanisms and thermochemical data have to be developed for all these applications. Few experimental studies have been reported. In pyrolysis, below 1000 K, Lhomme et al. [6] focused on the determination of the products of the reaction of different alkyl phosphates; Durig et al. [7] compared the reactivity of six compounds and proposed a decomposition mechanism by unimolecular eliminations. Zegers and Fisher studied the thermal decomposition of diethyl methylphosphonate (DEMP) [8], triethylphosphonate (TEP) [9] and diisopropyl methylphosphonate (DIMP) [10] in the temperature range 700-900 K. They measured the rate of the unimolecular reaction of the reactants and proposed mechanisms based on successive molecular eliminations. In combustion conditions, Werner and Cool [11] and Korobeinichev et al. [12] have studied

the effect of the addition of dimethyl methylphosphonate (DMMP) in a  $\text{H}_2/\text{O}_2$  flame; both have measured profiles of some phosphorus containing intermediates and products. The addition of trimethylphosphate (TMP) into a  $\text{H}_2/\text{O}_2$  flame have also been reported by Korobeinichev et al. [13] with a quantitative determination of the final phosphorus species [14-15].

Twarowski proposed a detailed mechanism in order to reproduce the effect of phosphine addition on the rate of recombination of H and OH [16]. It included 6 species and 33 reactions. The non-tabulated thermochemical data were evaluated by *ab initio* calculations. An extended version [17] was proposed involving 17 species and 162 reactions, reduced after analysis to 35 reactions. Werner and Cool proposed a mechanism of the combustion of DMMP [11] and used Twarowski's data for the small species. The thermochemistry data were evaluated by *ab initio* calculations.

The present work reports some evaluations of thermochemical data as group contributions and a kinetic study of the mechanism of decomposition of alkyl phosphate and phosphonate.

## Thermochemistry

The thermochemistry of phosphorus compounds is mostly unknown except for some small oxides. Since no experimental kinetic data are available, a postulated kinetic model will be strongly dependent of the estimation of the heat of formation and the entropy of the species. Benson [18] proposed some group additivity values for the estimation of the enthalpies, but not enough to allow to calculate all properties of all species involved in a detailed mechanism.

Melius performed some *ab initio* calculations with the BAC-MP4 method [19]. The heat of formation of some alkyl phosphates and alkyl phosphonates are reported, and also some evaluations of entropies and heat capacities [20]. By taking these data as a basis, an evaluation of group additivity contributions was done in order to be able to estimate easily and quickly the thermochemistry of a large number of phosphorus compounds. We focused on compounds involving a pentavalent phosphorus atom with a double bond with oxygen that is the common structure of species studied.

Six molecules of which enthalpies, entropies and heat capacities had been evaluated [20] allowed the estimation of six first groups. The optimization of the group contributions were performed by using as a first guess Benson's values [18] when available or, by analogy, the value of the corresponding group involving (CO) instead of (PO). Table 1 compares the new values of enthalpies with which ones proposed by Benson and Table 2 reports the heat of formation and entropy of the compounds used for the determination of the groups. As many other groups are needed, an evaluation of the properties of new species was done using the UHF/PM3 semi-empirical calculations of the MOPAC program [21]. Table 2 compares heats of formation calculated with the new group values, BAC-MP4 method, MOPAC and Benson's group values. Despite the worse precision of MOPAC evaluations, the difference of in the estimation of enthalpies is always less than  $10 \text{ kcal.mol}^{-1}$  or 6% and is below the error estimation given by Melius for his calculation [19] for these compounds. In the case of entropy and heat capacity, the evaluation done by MOPAC was corrected by the contribution of the internal rotors that

is not taken into account. The difference with BAC-MP4 calculations is less than  $8\text{ cal.mol}^{-1}$  or 8% for entropy. MOPAC evaluations always give higher values, and the difference seems to be related to the groups bonded to the (PO) group. Correction factors have been determined and applied to the further calculations. The corrections used are, for each substituent,  $-1.5\text{ cal.mol}^{-1}$  for OH,  $-1\text{ cal.mol}^{-1}$  for  $\text{CH}_3$  or  $\text{NH}_2$ ,  $-2\text{ cal.mol}^{-1}$  for  $\text{C}_2\text{H}_5$ ,  $-2.5\text{ cal.mol}^{-1}$  for  $\text{OCH}_3$ ,  $+3.3\text{ cal.mol}^{-1}$  for H, F or two of them.

Nineteen other group contributions are based on the evaluation of thermochemical data of new phosphorus compounds by MOPAC as described. They involved C, H, O, F, N, S and  $\text{C}\equiv\text{N}$  substituents. For some species, the heat of formation had been calculated by Melius [19]. The BAC-MP4 value was then preferred for the determination of the enthalpy contribution. This case occurred for the following groups :  $\text{PO}(\text{H})_2(\text{O})$ ,  $\text{PO}(\text{H})(\text{O})_2$ ,  $\text{PO}(\text{C})(\text{F})_2$ ,  $\text{PO}(\text{C})(\text{F})(\text{O})$ ,  $\text{PO}(\text{F})(\text{O})_2$ ,  $\text{PO}(\text{N})(\text{O})_2$ ,  $\text{C}(\text{C})(\text{H})_2(\text{PO})$ . Table 3 summarized all proposed group values.

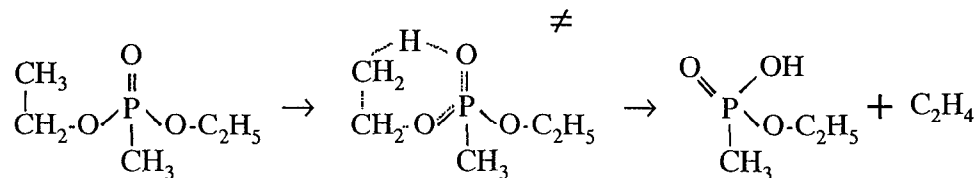
The thermochemical properties of radicals have been calculated from the data of the related molecule having an H-atom on the active site. Bond energies used for the enthalpies were deduced from the heat of formation of some radicals calculated by Melius [19]. The evaluation of entropies and heat capacities were performed by evaluating the change in the contribution of internal rotors and vibrations. Table 4 presents the data for some radicals involved in the DMMP and TEP oxidation.

The thermochemistry related to small species were taken from Melius calculations [19, 20] to ensure the coherence of the data in some cases where the reported evaluations are rather different [16, 20].

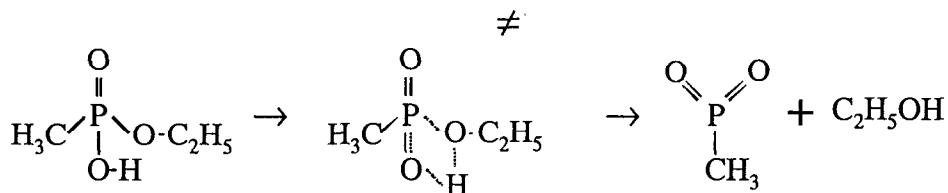
## Kinetic Model

### *Unimolecular decompositions*

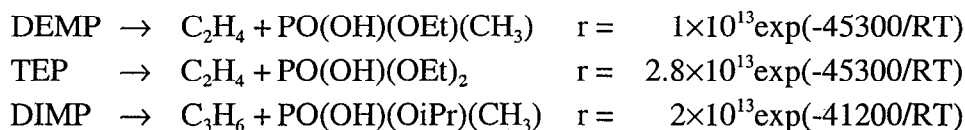
Two kinds of molecular decomposition seem to play a role in the degradation of alkyl phosphate or phosphonates. A six-center concerted reaction leads to the elimination of an alkyl substituent by producing an alkene. The reaction occurs by the formation of a cyclic transition state where an H-atom of the alkyl group is abstracted by the O-atom of the  $(\text{P}=\text{O})$  group.



The four-center reaction involves the abstraction of a H-atom from a OH substituent of the phosphorus by a O-atom that leads to the elimination of alcohol.



The rate of the six-center elimination have been measured by Zegers and Fisher for DEMP [8], TEP [9] and DIMP [10] by following the decay of the reactant in pyrolysis between 700 K and 900 K. The rates are, respectively,  $10^{14}\exp(-49100/RT)$ ,  $10^{14}\exp(-47400/RT)$  and  $10^{12}\exp(-36700/RT)$ . These rates are in good agreement with ones of decomposition of esters into acid and alkene that involves the same kind of transition state [10]. However, the measurements of esters decomposition shows that the pre-exponential factor A for such a six-member transition state is about  $10^{13}$  [10,18]. In the case of ethyl ester, A may be between  $3 \cdot 10^{12}$  and  $10^{13}$  [18]. Then we adopt the value of  $10^{13}$  for the DEMP decomposition, which has six abstractable H-atoms instead of three. Because of the loose of symmetries between the reactant and the transition state, A should be about two times higher for the reaction TEP and DIMP. The activation energies have been then corrected to fit with these A-factors. In the case of TEP, A is higher to keep the same activation energy as for DEMP. The rates are finally:

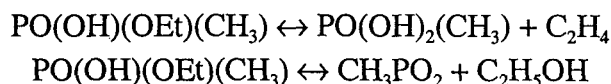


No experimental measurements have been reported for the four-center decomposition. In order to estimate these rates, a modeling of the experimental results of Zegers and Fisher was performed. Based of the analysis of the reaction products, alkene and alcohol, we suppose as these authors that no radical reaction occurs, but only successive six-center and four-center eliminations. The postulated mechanism is given in Table 5. The rate of the six-center decomposition of the mono and diesters produced from the reactants are the same as the first one after a correction of the A-factor for taking into account the number of alkyl groups. The rates of the four-center eliminations are then adjusted to reproduce the formation of alcohol and alkene.

The experimental results [8-10] were obtained in a flow reactor, at atmospheric pressure, with the reactant diluted in nitrogen. The profile of reactants and carbonated products were given. Products are ethylene and ethanol in the reaction of DEMP and TEP, and propene and *i*-propanol in the reaction of DIMP. Because of the importance of heterogeneous effects which change the ratio between the products [8-10], the initial load used for the calculations is for each species the amount extrapolated at  $t = 0$  at the lower temperature studied. This assumption supposes that the heterogeneous reactions are independent of the temperature and play a role in the entrance section of the flow reactor but may be neglected in the sampling probe. For the DIMP, the load used is exactly the initial one, but the start of the reaction is shifted by 10 ms.

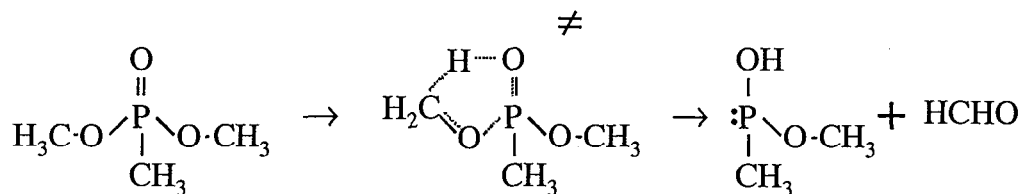
The pre-exponential factors for the four-center elimination are chosen to be in the same order as the corresponding reactions reported with carbonated compounds [18], then, respectively,  $2.5 \times 10^{13}$ ,  $3.5 \times 10^{13}$  and  $5 \times 10^{13}$  for the formation of ethanol, *i*-propanol and water. With such a value, the activation energy should be near the heat of reaction to be able to reproduce the experimental results, that is very different from other known reactions involving the same kind of transition state [18]. The activation energy of the reverse reaction of molecular addition of water or alcohol on a  $\text{PO}_2$  function is then very low, and should be below  $2 \text{ kcal.mol}^{-1}$ . In the TEP mechanism, because of the large uncertainty about the thermochemistry of  $\text{C}_2\text{H}_5\text{OPO}_2$ , the thermochemistry of the two reactions producing this compound and ethanol are taken equal to the corresponding elimination of ethanol in the DEMP mechanism.

Figure 1 compares the calculated ratios of alcohol and alkene to the experimental ones for the three reactants. For the highest conversions, obtained for long residence time, the alcohol production drops off in agreement with experimental results. The four-center eliminations reactions are indeed near the equilibrium; the concurrent elimination of alkene leads to the consumption of alkyl phosphate or phosphonate and the shift in the equilibrium favors then the reverse reaction of addition of alcohol; for instance, in the DEMP mechanism:



Figures 2-4 show reactants and carbonated products profiles for, respectively, the pyrolysis of DEMP, TEP and DIMP. Figure 5 presents the computed profiles of the phosphorus products for the reaction of DIMP. The most important one is  $\text{CH}_3\text{PO}_2$  which is in equilibrium with water and *i*-propanol.

A five-center elimination producing a compound with trivalent phosphorus seems to be possible and could explain the high reactivity of alkylphosphine oxides [7]; but the cyclic transition state does not allow a concerted reaction and the activation energy is too high to give a significant role to this reaction in the case of alkyl phosphate or phosphonate. For the reaction of DMMP :



Werner and Cool [11] propose an activation energy of  $87.3 \text{ kcal.mol}^{-1}$ , based on BAC-MP4 calculations.

### Combustion model

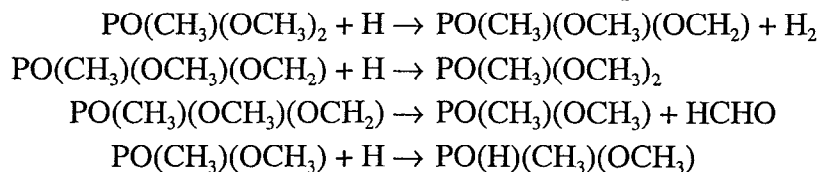
A mechanism has been built in order to reproduce the combustion of the DMMP. It includes reaction types usually considered in the combustion of hydrocarbons and the molecular eliminations. The molecular intermediates taken into account are  $\text{PO(OH)(OCH}_3)_2$ ,  $\text{PO(OH)(CH}_3)(\text{OCH}_3)$ ,  $\text{PO(OH)}_2(\text{OCH}_3)$ ,  $\text{PO(OH)}_2(\text{CH}_3)$ ,  $\text{PO(OH)}_3$ ,

CH<sub>3</sub>PO, CH<sub>3</sub>OPO and CH<sub>3</sub>PO<sub>2</sub>. These compounds can react by molecular elimination, bond scission, H-abstraction by O<sub>2</sub> or a free radical and addition of H or OH on the P=O double bond. The radicals produced then react by combination with small free radicals or by decomposition involving a bond-breaking in β-position of the active center. The ultimate products are HOPO, HOPO<sub>2</sub>, HPO, HPO<sub>2</sub>, PO, PO<sub>2</sub>, and PO<sub>3</sub>. For these species, all unimolecular and bimolecular possible reactions are written by considering also reactions with H, O, OH, HO<sub>2</sub>, H<sub>2</sub>O and CH<sub>3</sub>. The complete mechanism consists of 35 different chemical species and 263 reactions. The kinetic data were estimated by analogy with reactions of carbon or nitrogen containing species and by thermochemical considerations.

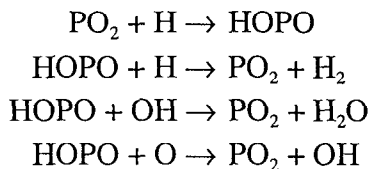
The mechanism used for modeling the combustion of oxygenated and carbonated species is issued from a mechanism of combustion of dimethylether [22]. We just kept the part related of species containing two or less C-atoms, that consists of 51 species and 263 reactions.

This mechanism has been used to model the combustion of DMMP added in a H<sub>2</sub>/O<sub>2</sub>/Ar stabilized premixed stoichiometric flame in the experimental conditions of Korobeinichev [12]. The calculation were performed with the PREMIX [23] code of the Sandia National Laboratory. Figure 6 compare the computed and experimental temperature profile of the flame with and without the adjunction of 0.2% of DMMP. The increased heat release when the DMMP is added is well reproduced by the model. Figure 7 and 8 show the computed profiles of the phosphorus compounds. The DMMP is quickly consumed in the first stage of the flame. Intermediates as alkyl phosphates and phosphonates are produced after an H-abstraction or an addition of H on the P=O bond. These very reactive species lead fast, mostly by molecular elimination, to the formation of small compounds. These are orthophosphoric acid, which gives HOPO<sub>2</sub> when the temperature increases, HOPO, HOPO<sub>2</sub> and the radicals PO and PO<sub>2</sub>.

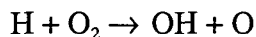
The increased heat release when the DMMP is added is well reproduced by the model. The higher temperature is due to the raise of the exothermic combinations reactions induced by the phosphorus species. In the very beginning of the flame, a termination cycle appears with H-abstractions on the DMMP followed by combination of the produced radical or the radicals produced after a decomposition :



Later, the major effect comes from the cycle already proposed by Twarowski [17] that involves PO<sub>2</sub>:



Despite the drop of radical concentration in the flame caused by the combinations, the higher temperature leads to a strong acceleration of the combustion by the way of the branching reaction:



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**Table 1** : Enthalpy value of groups determined using BAC-MP4 data.

$\Delta H_f^\circ$ (kcal.mol <sup>-1</sup> )		
Group	This study	Benson [18]
PO-(C)(O) <sub>2</sub>	-92.7	-99.5
PO-(C)(H)(O)	-74.3	-
PO-(O) <sub>3</sub>	-106.4	-104.6
C-(H) <sub>3</sub> (PO)	-9.95	-10.08
O-(C)(PO)	-36.8	-40.7
O-(H)(PO)	-54.9	-65.0

**Table 2** : Entalpy and entropy of selected compounds.

$\Delta H_f^\circ$ (kcal.mol <sup>-1</sup> )				
Species	This study	BAC-MP4 [20]	MOPAC calculations	Benson [18]
PO(CH <sub>3</sub> )(OCH <sub>3</sub> ) <sub>2</sub>	-196.4	-196.4	-189.2	-211.1
PO(H)(CH <sub>3</sub> )(OCH <sub>3</sub> )	-131.1	-131.5	-134.1	-
PO(OH)(CH <sub>3</sub> )(OCH <sub>3</sub> )	-204.4	-206.7	-195.6	-225.4
PO(OH)(OCH <sub>3</sub> ) <sub>2</sub>	-255.1	-255.6	-250.6	-271.2
PO(OH) <sub>3</sub>	-271.1	-272.3	-270.2	-299.6
PO(OH) <sub>2</sub> (CH <sub>3</sub> )	-212.4	-210.9	-209.1	-239.6
$S^\circ$ (cal.mol <sup>-1</sup> )				
Species	This study	BAC-MP4 [20]	MOPAC calculations <sup>a</sup>	
PO(CH <sub>3</sub> )(OCH <sub>3</sub> ) <sub>2</sub>	99.1	98.6	100.4	
PO(H)(CH <sub>3</sub> )(OCH <sub>3</sub> )	85.4	85.1	85.1	
PO(OH)(CH <sub>3</sub> )(OCH <sub>3</sub> )	90.5	92.1	91.7	
PO(OH)(OCH <sub>3</sub> ) <sub>2</sub>	100.5	100.5	99.9	
PO(OH) <sub>3</sub>	81.3	81.3	82.0	
PO(OH) <sub>2</sub> (CH <sub>3</sub> )	82.0	81.2	83.0	

<sup>a</sup> After correction for internal rotors contribution and bond-correction (see text).

**Table 3** : Group contributions for organophosphorus compounds.

Group	$\Delta H_f^\circ$	$S^\circ$	$C_p^\circ$ (cal.K <sup>-1</sup> .mol <sup>-1</sup> )					
	kcal.mol <sup>-1</sup>	cal.K <sup>-1</sup> .mol <sup>-1</sup>	298 K	300 K	500 K	800 K	1000 K	1500 K
PO-(C)(H)(O)	-74.3	23.1	9.5	12.6	15.4	16.1	16.1	
PO-(C)(O) <sub>2</sub>	-92.7	0.3	9.3	12.2	13.2	13.3	13.4	
PO-(O) <sub>3</sub>	-106.4	-0.2	9.1	11.6	12.9	13.2	13.2	
PO-(H) <sub>2</sub> (O)	-69.1	39.7	9.5	14.2	18.2	19.5	21.5	
PO-(H)(O) <sub>2</sub>	-91.1	19.2	9.3	12.5	14.8	15.6	17.5	
PO-(C)(F)(H)	-138.0	49.3	12.1	14.7	18.2	19.0	22.7	
PO-(C)(F) <sub>2</sub>	-215.1	55.3	16.5	19.2	20.7	21.0	21.3	
PO-(C)(F)(O)	-161.6	24.7	11.4	14.6	16.1	16.5	19.7	
PO-(F)(O) <sub>2</sub>	-173.1	20.6	12.1	15.4	16.6	17.0	18.2	
PO-(F)(H)(O)	-157.5	47.7	12.6	16.8	19.9	21.9	22.1	
PO-(CN)(C)(O)	-46.3	30.9	15.4	18.8	20.5	21.0	25.0	
PO-(C)(N)(O)	-70.3	4.8	9.9	11.6	11.6	11.5	13.0	
PO-(N)(O) <sub>2</sub>	-94.5	-0.5	9.6	11.8	12.3	12.3	11.7	
PO-(CN)(N)(O)	-42.0	33.7	17.1	19.6	20.5	20.9	20.6	
PO-(C)(O)(S)	-63.9	1.6	6.9	9.8	11.6	12.4	16.1	
C-(H) <sub>3</sub> (PO) <sup>a</sup>	-9.95	28.1	6.19	9.4	13.03	14.77	14.9	
C-(C)(H) <sub>2</sub> (PO)	-5.2	3.0	3.9	7.6	9.8	12.1	13.4	
O-(H)(PO)	-54.9	27.9	4.7	5.5	6.4	6.8	7.1	
O-(C)(PO)	-36.8	8.2	2.8	3	3.4	3.6	3.6	
O-(PO) <sub>2</sub>	-56.4	1.8	6.2	6.3	6.4	6.5	8.4	
N-(H) <sub>2</sub> (PO) <sup>b</sup>	-14.9	24.69	4.07	7.13	9.96	11.22	14.5	
N-(C)(H)(PO)	-3.2	4.4	3.1	5.8	8.0	8.9	11.5	
N-(C) <sub>2</sub> (PO)	8.6	-17.3	4.5	7.2	8.7	8.9	11.5	
S-(H)(PO) <sup>c</sup>	-1.4	31.2	7.63	8.12	8.5	8.24	8.2	
S-(C)(PO)	6.4	11.3	5.4	5.5	5.1	4.4	3.9	

<sup>a</sup> C-(H)<sub>3</sub>(PO)  $\equiv$  C-(H)<sub>3</sub>(CO) assigned for C<sub>p</sub><sup>o</sup><sup>b</sup> N-(H)<sub>2</sub>(PO)  $\equiv$  N-(H)<sub>2</sub>(CO) assigned<sup>c</sup> S-(H)(PO)  $\equiv$  S-(H)(CO) assigned

**Table 4 : Thermochemical properties of selected radicals**

Species	$\Delta H_f^\circ$	$S^\circ$	$C_p^\circ$ (cal.K <sup>-1</sup> .mol <sup>-1</sup> )				
	kcal.mol <sup>-1</sup>	cal.K <sup>-1</sup> .mol <sup>-1</sup>	300	500	800	1000	1500
PO(H)(OH)	-85.6	66.7	13.9	18.2	21.6	22.6	23.9
PO(OH) <sub>2</sub> (CH <sub>2</sub> )	-158.9	85.5	25.4	31.9	36.4	38.4	41.5
PO(OH) <sub>2</sub> (OCH <sub>3</sub> )	-264.5	88.0	26.5	35.0	42.1	45.1	50.0
PO(OH) <sub>2</sub> (OCH <sub>2</sub> )	-215.9	90.1	26.3	33.8	39.6	41.9	45.6
PO(OH)(CH <sub>3</sub> )	-100.4	75.9	19.9	25.7	31.6	33.8	35.0
PO(OH)(OCH <sub>3</sub> )	-143.5	81.8	22.5	28.6	34.4	36.9	40.0
PO(OCH <sub>3</sub> ) <sub>2</sub>	-137.5	93.0	26.1	35.5	44.4	48.4	55.0
PO(OH)(CH <sub>3</sub> )(OCH <sub>2</sub> )	-158.0	94.1	28.9	38.5	46.4	50.0	55.6
PO(OH)(OCH <sub>3</sub> )(CH <sub>2</sub> )	-153.9	95.4	28.9	38.5	46.4	50.0	55.6
PO(CH <sub>3</sub> )(OCH <sub>3</sub> )O	-137.1	89.0	28.3	37.5	46.3	50.2	56.2
PO(CH <sub>3</sub> )(OCH <sub>3</sub> )(OCH <sub>2</sub> )	-147.8	100.7	31.6	43.2	55.2	60.4	68.5
PO(CH <sub>2</sub> )(OCH <sub>3</sub> ) <sub>2</sub>	-143.6	101.9	31.6	43.2	55.2	60.4	68.5
PO(OCH <sub>3</sub> ) <sub>2</sub> (OCH <sub>2</sub> )	-198.3	109.0	35.9	47.7	59.6	65.0	72.4

**Table 5 : Pyrolysis mechanism of DEMP, DIMP and TEP**

Reaction	A	b	E
DEMP $\leftrightarrow$ PO(OH)(OEt)(CH <sub>3</sub> ) + C <sub>2</sub> H <sub>4</sub>	$1 \times 10^{13}$	0	45300
PO(OH)(OEt)(CH <sub>3</sub> ) $\leftrightarrow$ PO(OH) <sub>2</sub> (CH <sub>3</sub> ) + C <sub>2</sub> H <sub>4</sub>	$5 \times 10^{12}$	0	45300
PO(OH)(OEt)(CH <sub>3</sub> ) $\leftrightarrow$ CH <sub>3</sub> PO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> OH	$2.5 \times 10^{13}$	0	44000
PO(OH) <sub>2</sub> (CH <sub>3</sub> ) $\leftrightarrow$ CH <sub>3</sub> PO <sub>2</sub> + H <sub>2</sub> O	$5 \times 10^{13}$	0	39000
DIMP $\leftrightarrow$ PO(OH)(OiPr)(CH <sub>3</sub> ) + C <sub>3</sub> H <sub>6</sub>	$2 \times 10^{13}$	0	41200
PO(OH)(OiPr)(CH <sub>3</sub> ) $\leftrightarrow$ PO(OH) <sub>2</sub> (CH <sub>3</sub> ) + C <sub>3</sub> H <sub>6</sub>	$1 \times 10^{13}$	0	41200
PO(OH)(OiPr)(CH <sub>3</sub> ) $\leftrightarrow$ CH <sub>3</sub> PO <sub>2</sub> + C <sub>3</sub> H <sub>7</sub> OH	$3.5 \times 10^{13}$	0	43000
TEP $\leftrightarrow$ PO(OH)(OEt) <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	$2.8 \times 10^{13}$	0	45300
PO(OH)(OEt) <sub>2</sub> $\leftrightarrow$ PO(OH) <sub>2</sub> (OEt) + C <sub>2</sub> H <sub>4</sub>	$1.9 \times 10^{13}$	0	45300
PO(OH)(OEt) <sub>2</sub> $\leftrightarrow$ C <sub>2</sub> H <sub>5</sub> OPO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> OH	$2.5 \times 10^{13}$	0	44000
PO(OH) <sub>2</sub> (OEt) $\leftrightarrow$ PO(OH) <sub>3</sub> + C <sub>2</sub> H <sub>4</sub>	$9.6 \times 10^{12}$	0	45300
PO(OH) <sub>2</sub> (OEt) $\leftrightarrow$ HOPO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> OH	$2.5 \times 10^{13}$	0	44000
C <sub>2</sub> H <sub>5</sub> OPO <sub>2</sub> $\leftrightarrow$ HOPO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	$1.9 \times 10^{13}$	0	45300
PO(OH) <sub>2</sub> (OEt) $\leftrightarrow$ C <sub>2</sub> H <sub>5</sub> OPO <sub>2</sub> + H <sub>2</sub> O	$5 \times 10^{13}$	0	45000
PO(OH) <sub>3</sub> $\leftrightarrow$ HOPO <sub>2</sub> + H <sub>2</sub> O	$1.5 \times 10^{14}$	0	46000

Units are mol, cm<sup>3</sup>, s, K and cal/mol.

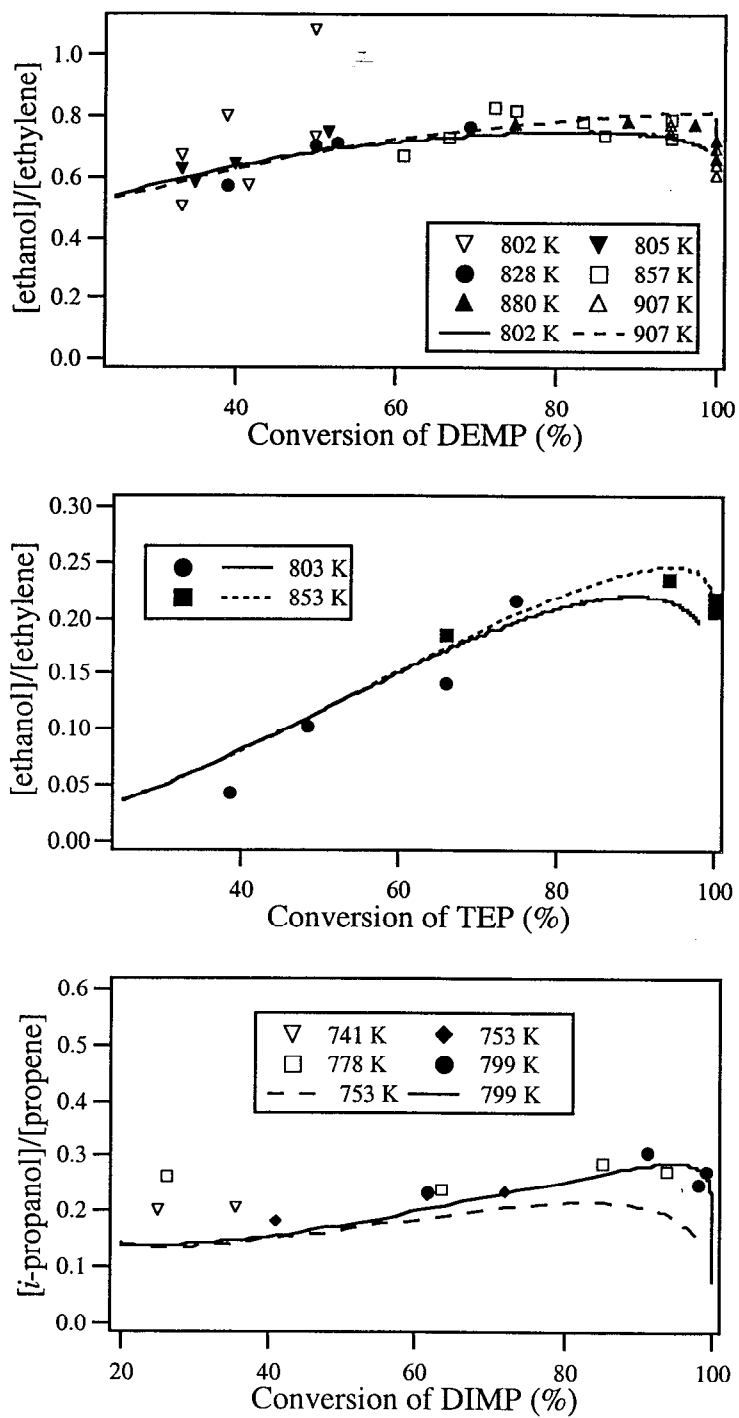


Figure 1: Ratio of alcohol and alkene amount formed in the pyrolysis of DEMP [8], TEP [9] and DIMP [10]. Lines are model predictions.

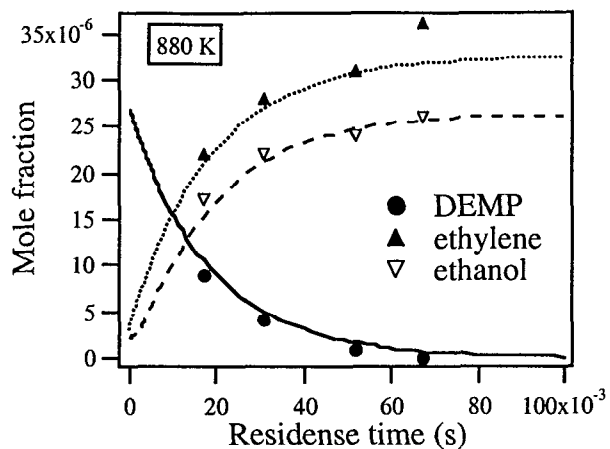


Figure 2: Profile of species in the pyrolysis of DEMP at 880 K [8]. Lines are model predictions.

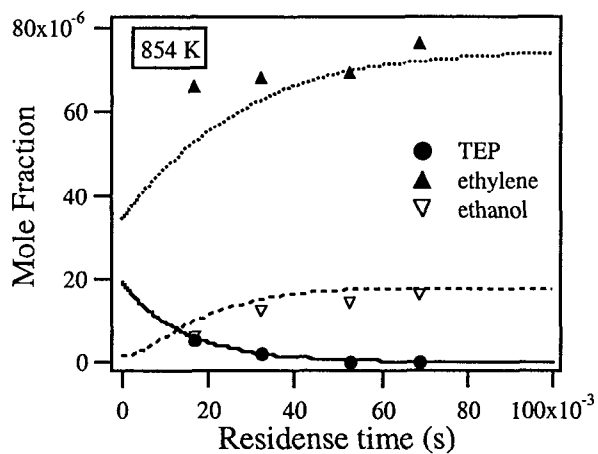


Figure 3: Profile of species in the pyrolysis of TEP at 854 K [9]. Lines are model predictions.

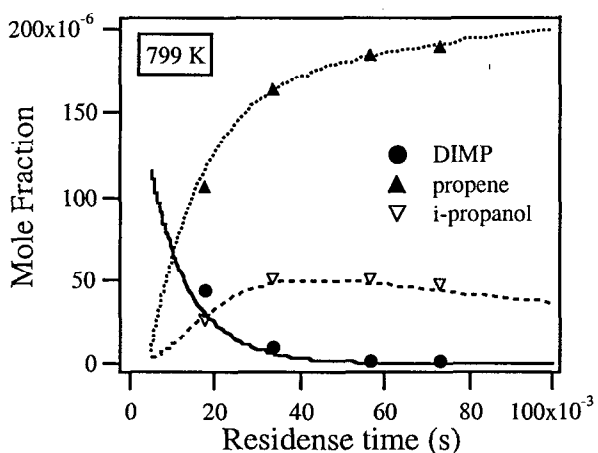


Figure 4: Profile of species in the pyrolysis of DIMP at 799 K [10]. Lines are model predictions.

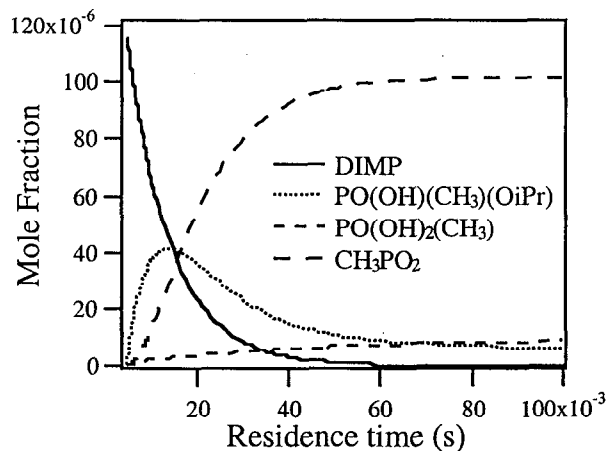


Figure 5: Computed profile of the phosphorus compounds in the pyrolysis of DIMP at 799 K in the conditions of [10].

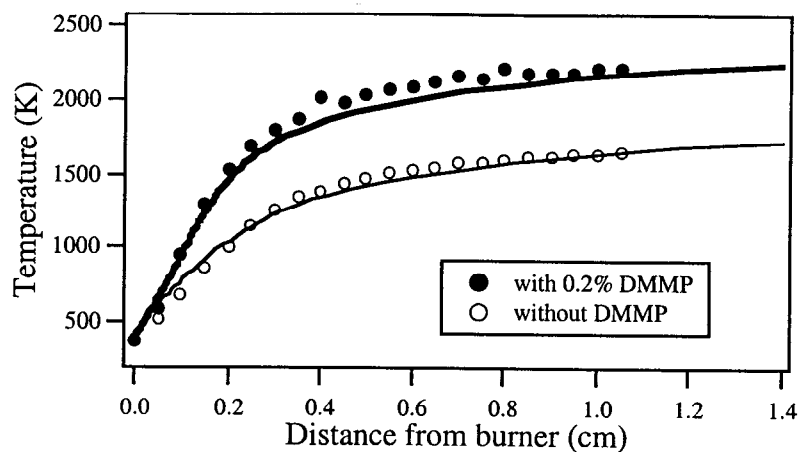


Figure 6: Experimental and computed profile of the temperature in the stoichiometric premixed  $\text{H}_2/\text{O}_2/\text{Ar}$  flame [10].

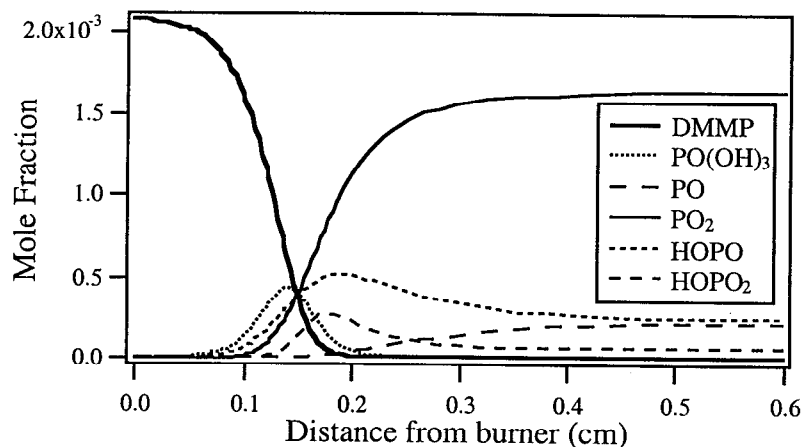


Figure 7: Computed profile of DMMP and final phosphorus species in the stoichiometric premixed  $\text{H}_2/\text{O}_2/\text{Ar}$  flame [10].

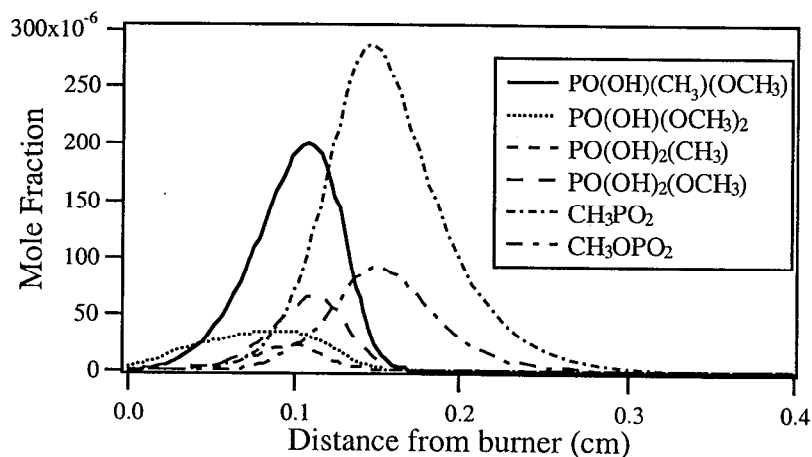


Figure 8: Computed profile of intermediate phosphorus species in the stoichiometric premixed  $\text{H}_2/\text{O}_2/\text{Ar}$  flame [10].